PCT

WORLD INTELLECTUAL
Internati

INTERNATIONAL APPLICATION PUBLISHED UN

WO 9602136A1

(51) International Patent Classification 6 :
A01N 25/04, 25/28, B01F 3/08, B01J 13/14

A1

(11) International Publication Number: WO 96/02136

(43) International Publication Date: 1 February 1996 (01.02.96)

(21) International Application Number: PCT/US95/08817

(22) International Filing Date: 13 July 1995 (13.07.95)

(30) Priority Data:
9414318.7 15 July 1994 (15.07.94) GB

(71) Applicant (*for all designated States except US*): DOWELANCO LIMITED [US/US]; 9330 Zionsville Road, Indianapolis, IN 46268 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): MULQUEEN, Patrick, J. [GB/GB]; 8 Sewell Close, Abingdon, Oxen OX14 3YJ (GB). LUBETKIN, Steven, D. [GB/GB]; 24 Haywards Close, Wantage, Oxen OX12 7AT (GB). SMITH, Geoffrey, W. [GB/GB]; Wistgria Cottage, S. New Row, Buckland, Oxen SN78 02N (GB). PATERSON, Eric, S. [GB/GB]; 14 Vicarage Close, Grove, Wantage, Oxfordshire OX12 7NS (GB).

(74) Agent: SICKERT, Dugal, S.; DowElanco, 9330 Zionsville Road, Indianapolis, IN 46268 (US).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CZ, EE, FI, GB, GE, HU, IS, JP, KG, KR, KZ, LK, LR, LT, LV, MD, MG, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PREPARATION OF AQUEOUS EMULSIONS

(57) Abstract

A method of controlling the particle size and particle size distribution of an aqueous emulsion having a non-aqueous disperse phase during the production thereof, in which the production of the emulsion is carried out in the presence of a dispersion of a templating agent, such as a polymer latex, and surfactant. Particle size and particle size distribution of the dispersion is controlled by selecting the templating agent and surfactant such as to cause deposition of the disperse phase on particles of the dispersed templating agent, such that the particle size distribution of the templating agent provides a template for the particle size distribution of the final emulsion.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**GB**	United Kingdom	**MR**	Mauritania
AU	Australia	**GE**	Georgia	**MW**	Malawi
BB	Barbados	**GN**	Guinea	**NE**	Niger
BE	Belgium	**GR**	Greece	**NL**	Netherlands
BF	Burkina Faso	**HU**	Hungary	**NO**	Norway
BG	Bulgaria	**IE**	Ireland	**NZ**	New Zealand
BJ	Benin	**IT**	Italy	**PL**	Poland
BR	Brazil	**JP**	Japan	**PT**	Portugal
BY	Belarus	**KE**	Kenya	**RO**	Romania
CA	Canada	**KG**	Kyrgystan	**RU**	Russian Federation
CF	Central African Republic	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CG	Congo			**SE**	Sweden
CH	Switzerland	**KR**	Republic of Korea	**SI**	Slovenia
CI	Côte d'Ivoire	**KZ**	Kazakhstan	**SK**	Slovakia
CM	Cameroon	**LI**	Liechtenstein	**SN**	Senegal
CN	China	**LK**	Sri Lanka	**TD**	Chad
CS	Czechoslovakia	**LU**	Luxembourg	**TG**	Togo
CZ	Czech Republic	**LV**	Latvia	**TJ**	Tajikistan
DE	Germany	**MC**	Monaco	**TT**	Trinidad and Tobago
DK	Denmark	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**US**	United States of America
FI	Finland	**ML**	Mali	**UZ**	Uzbekistan
FR	France	**MN**	Mongolia	**VN**	Viet Nam
GA	Gabon				

PREPARATION OF AQUEOUS EMULSIONS

This invention relates to the preparation of aqueous emulsions and in particular to the preparation of such emulsions having predictable particle sizes and/or predictable particle size distribution.

The method is particularly suitable for the production of agricultural compositions, for example pesticidal emulsions and the like, having controlled particle size distribution, although it also finds application in various other situations in which controlled particle size emulsions are required either as an end product, or as an intermediate in the production of other products such as microspheres or the like.

In accordance with the invention, we have discovered that an aqueous emulsion having a non-aqueous disperse phase with a controlled particle size distribution can be produced by employing during the production of the emulsion a material such as a latex or a dispersion of a particulate solid, which has a known particle size and/or particle size distribution, the particles of which will form a template for the particle size and/or particle size distribution of the resulting aqueous emulsion. Such materials are referred to herein as "templating agents".

The templating agents suitable for use in the present invention are any materials which will provide, in the presence of appropriate surfactants, a template for the formation of the desired emulsion. Inorganic fillers and the like may be employed as the templating agent, but it is particularly preferred that the templating agent should be a polymer dispersion, particularly an aqueous latex, since

it is a relatively straightforward procedure to produce latex particles in predictable particle sizes, and particle size distributions.

The templating agent may be utilised in the production of the aqueous emulsion of the invention in a number of ways. In a preferred embodiment, an emulsion of the disperse phase component(s) of the final emulsion is prepared, using appropriate surfactants, in the presence of the templating agent. In an alternative embodiment, an emulsion may be prepared of the components intended to constitute the disperse phase of the final emulsion, and this emulsion is then combined with the templating agent, in the presence of an appropriate surfactant.

The templating agent and surfactant are chosen such that deposition of the disperse phase of the emulsion takes place on the particles of the dispersed templating agent. The particle size distribution of the templating agent thus provides a template for the particle size distribution of the resulting emulsion.

By this method, the particle size distribution of the resulting aqueous emulsion can be controlled by appropriate control of the particle size distribution of the templating agent.

It is very difficult by conventional methods to produce emulsions with particle sizes and particle size distributions which are both easily reproducible, and easily controlled. By contrast, many of the templating agents which can be employed in accordance with the present invention can easily be produced in particle size distributions which are easy to control, and in particular which have a narrow particle size distribution, or which

have a multimodal (e.g., a bimodal) particle size distribution.

The surprising finding on which the present invention is based is that when the templating agent is employed, the shape of the particle size distribution of the resulting aqueous emulsion reflects very closely the shape of the particle size distribution of the templating agent employed. In particular, when a templating agent having a narrow particle size distribution is employed, the particle size distribution of the emulsion produced is correspondingly narrow.

WO89/03135 discloses methods for preparing stabilized water-diluable pesticide compositions, in which latexes are employed as a stabilizing agent. However, there is no suggestion in this reference that the particle size distribution of the stabilizing latex can provide a template for the particle size distribution of the final emulsion. Neither is there any suggestion of the possibility of producing emulsions which are either substantially monodisperse, or multimodal.

EP-A-0483416 discloses the preparation of aqueous latex compositions loaded with various materials, for example dyes and optical brighteners. Again, there is no suggestion that the particle size <u>distribution</u> of the latex can be used to provide a template for a resulting polymeric emulsion. Likewise, there is no suggestion of the preparation either of monodisperse or of multimodal emulsions.

Accordingly, in a first aspect of the invention, there is provided a method of controlling the particle size and particle size distribution of an aqueous emulsion having a

non-aqueous disperse phase, during the production thereof, wherein the production of the emulsion is carried out in the presence of a dispersion of a templating agent and surfactant and wherein the control of particle size and particle size distribution of the emulsion is controlled by selecting the templating agent and surfactant such as to cause deposition of the disperse phase on particles of the dispersed templating agent, such that the particle size distribution of the templating agent provides a template for the particle size distribution of the final emulsion.

The breadth of the particle size distribution of a dispersion may be characterized in a number of ways. For particles with a median particle size of greater than about 0.5 micrometer, the breadth of the particle size distribution is typically characterised by "span", defined as

$$\text{span} = \frac{D(90) - D(10)}{D(50)},$$

wherein D(10), D(50) and D(90), represent respectively the particle diameters at the 10%, 50% and 90% points in the volume fraction distribution curve. Such measurements may be carried out using laser diffraction techniques, for example using a Malvern Mastersizer™ instrument.

For particles with a median particle size of less than about 0.5 micrometer, breadth of the particle size distribution is typically characterised by "polydispersity", using photon correlation spectroscopy techniques, for example using a Malvern Zetasizer™ or Malvern Hi-C™ instrument. Polydispersity can be derived from the experimentally determined correlation function which is measured by this technique.

To determine the polydispersity, the measured correlation function Y(t) is fitted to a power series

$$Y(t)=A + Bt + Ct^2 + \ldots\ldots$$

where t is the delay time, and polydispersity is then defined as

$$\frac{C}{B^2}$$

For particle sizes of around 0.5 micrometer, either photon correlation spectroscopy or laser diffraction techniques may be employed (although the results measured by the two techniques may not agree absolutely in every case).

The term "monodisperse" as used herein is intended to mean either a dispersion which fulfils the requirement <u>either</u> that its span (as defined above) has a value of 2 or less, preferably 1 or less, <u>or</u> that it has a polydispersity (measured as indicated above) of 0.15 or less, preferably 0.1 or less.

In accordance with the present invention, the templating agent, and thus the resulting aqueous emulsion, is preferably monodisperse as defined above.

Accordingly, in a second aspect of the invention, there is provided a method of producing an aqueous emulsion having a disperse non-aqueous phase with a substantially monodisperse particle size distribution, wherein the production of the emulsion is carried out in the presence of a dispersion of a templating agent and surfactant

wherein the templating agent has a substantially monodisperse particle size distribution, and wherein the nature and amount of the surfactant is such as to cause deposition of the disperse phase on particles of the dispersed templating agent, such that the particle size distribution of the templating agent provides a template for the particle size distribution of the resulting emulsion.

In an alternative embodiment, the templating agent may be prepared so as to have a multimodal, for example a bimodal particle size distribution. By this method, it is possible to prepare aqueous emulsions which reflect the same multimodal or bimodal particle size distributions.

Accordingly, in a further aspect of the invention, there is provided a method of producing an aqueous emulsion having a dispersed non-aqueous phase with a multimodal particle size distribution, wherein the production of the emulsion is carried out in the presence of a dispersion of a templating agent and surfactant wherein the templating agent has a multimodal particle size distribution, and wherein the nature and amount of the surfactant is such as to cause deposition of the disperse phase on particles of the dispersed templating agent, such that the particle size distribution of the templating agent provides a template for the particle size distribution of the resulting emulsion.

As will be described in more detail hereinafter, emulsions prepared in accordance with the present invention can be used in the preparation of microcapsules and the like. Although many techniques exist for the production of microcapsules, it is in general difficult to produce microcapsules of small particle size (e.g. less than 5000

nm), which are substantially monodisperse. Accordingly, in a further preferred embodiment of this invention, the templating agent may have an average particle size of 5000 nm or less.

As indicated above, the term "dispersion" as used herein in connection with the compositions of the invention is intended to include within its scope both emulsions of essentially liquid materials, prepared employing the said templating agent and surfactant, and dispersions of solid particles. Such solid dispersions can be obtained, for example, by preparing an emulsion as previously described, and then causing the emulsion particle to solidify by various means.

The nucleating agents suitable for use in the present invention are any materials which will provide, in the presence of appropriate surfactants, a template for the formation of the desired emulsion. Inorganic fillers and the like may be employed as the templating agent, but it is particularly preferred that the templating agent should be a polymer dispersion, particularly an aqueous latex,

The term "latex" as used herein is intended to mean any stable suspension of polymer particles in water. Particular examples are polymer suspensions produced in an aqueous suspension emulsion polymerization process, and post-dispersed suspensions, such polyurethanes and ethyl cellulose dispersions.

Suitable latexes for use as templating agents in accordance with the present invention preferably have a particle size of from 30 to 20,000 nm, more preferably from 100 to 5,000 nm.

Preferred latexes comprise polymers and copolymers of styrene, alkyl styrenes, isoprene, butadiene, acrylonitrile lower alkyl acrylates, vinyl chloride, vinylidene chloride, vinyl esters of lower carboxylic acids and alpha, beta-ethylenically unsaturated carboxylic acids, including polymers containing three or more different monomer species copolymerized therein, the size of the polymeric particles being in the range of from 30 to 20,000 nm, preferably from 100 to 5,000 nm. Small amounts for example 0 to 10 percent of bifunctional monomers may be employed to crosslink the polymers if desired.

The latex may be present when the initial emulsion is formed, in which case the emulsion droplets will begin to combine with the latex immediately they are formed. Alternatively, an emulsion may first be formed by combination of the eventual disperse phase with the surfactant, in the presence of water, and the emulsion thus formed may thereafter be combined with the latex. It is found that the increase in particle size diameter which occurs is that which might be expected if deposition takes place entirely on the surface of the particles of the templating agent.

Although the applicant does not wish to be bound by any particular theory of preparation of the present invention, it is believed that initially incorporation of the disperse phase into the templating agent does not take place by the mechanism of swelling or imbibition. Thus, the increase in particle size due to deposition of the disperse phase on the templating agent can be readily calculated by reference to the known particle size and size distribution of the templating agent, and the quantity of the disperse phase which is added.

Surprisingly it is found that the volume of disperse phase which can be deposited in this way is very large, in comparison with the overall volume of the templating agent. Typically, the volume ratio of the disperse phase to the templating agent can be as high as 100:1, with volume ratios of 10:1 (resulting in an increase in size by a factor of around 2.2 in the templating agent particles) being rapidly and easily achievable.

The disperse phase may preferably take the form of a solution in an appropriate solvent of the material of which it is desired to form the emulsion. For example, the method of the invention may be used to produce pesticidal emulsions, by forming a solution of a pesticide in appropriate water-immiscible solvent, and subsequently emulsifying the solvent, together with appropriate surfactants, in the presence of the templating agent.

Alternatively, the disperse phase may take the form of a single chemical compound, which is liquid at normal temperatures or is heated to a temperature at which it is molten. A suitable example of the latter is the pesticide chlorpyrifos, which can in accordance with the invention be produced in uniform and small particle size distribution.

When a water-immiscible solvent is employed, the nature of the water-immiscible solvent will vary depending upon the nature of any substances which it is desired to incorporate, and the nature of the templating agent. Specific examples however are the aromatic liquids, particularly alkyl substituted benzenes such as xylene or propyl benzene fractions, and mixed naphthalene and alkyl naphthalene fractions; mineral oils, substituted aromatic organic liquids such as dioctyl phthalate; kerosene, polybutenes; dialkylamides of various fatty acids,

particularly the dimethyl amides of fatty acids such as the dimethyl amide of caprylic acid; chlorinated aliphatic and aromatic hydrocarbons such as 1,1,1-trichloroethane and chlorobenzene, esters of glycol derivatives, such as the acetate of the n-butyl, ethyl, or methyl ether of diethyleneglycol, the acetate of the methyl ether of dipropyleneglycol, ketones such as isophorone and trimethylcyclohexanone (dihydorisophorone) and the acetate products such as hexyl-, or heptylacetate, and the solvents derived from vegetable oils such as the fatty acid esters, for example methyl oleate. Preferred organic liquids are xylene, propyl benzene fractions, dihydroisophorone, and methyl oleate.

The solvent may, in accordance with a preferred embodiment of the invention, be a volatile material, for example a volatile hydrocarbon such as propane or butane. By this method, the volatile solvent may be volatilized after deposition, leaving behind controlled amounts of solute. The solute may be, for example, a pesticidal material, and may in one embodiment include a film-forming polymer, such that a polymer shell is formed on volatilization of the volatile solvent.

Alternatively, the disperse phase may include reactive monomers, oligomers, or pre-polymers, to facilitate the production of microcapsules and the like from the dispersed particles.

Emulsions prepared in accordance with the present invention appear to be stable over long periods of time, even at very high internal phase volume fractions. The diameter of the disperse phase particles can easily be determined by simple calculation based on the templating agent particle size and the amount of non-aqueous phase

employed.

Emulsions in accordance with the present invention may find application, for example, in the manufacture of fuel emulsions and the like, which burn more uniformly, and with less harmful emissions, if the aerosol droplet size is monodisperse.

The predictable manner in which coating of the templating agent particles takes place makes it possible to deliver accurately very small amounts of active materials, by, for example, employing low concentrations of the active materials in the non-aqueous phase used to produce the emulsion, and subsequently evaporating the solvent used.

Similarly, by using the techniques previously described employing polymerizable monomers and the like, and subsequently polymerizing the monomer, oligomer, or pre-polymer, core/shell particles can be produced with wall thicknesses which can be controlled very accurately, simply by calculation of the anticipated deposition thickness of the non-aqueous phase, and a knowledge of the concentration of the monomer employed.

The non-aqueous phase employed in the production of such microcapsules may contain chosen amounts of plasticizer for the wall of the finished capsule, thus enabling control of the release kinetics of the finished microcapsules.

In yet a further embodiment, a material can be included within the non-aqueous phase which can be made to react with the continuous phase, either spontaneously after a period of time, or upon alteration of some appropriate parameter of the continuous phase, for example the pH,

ionic strength, or the addition of a further reactant. For example, organic derivatives of silicate, titanates, zirconates, and the like, can be employed in the non-aqueous phase, and subsequently hydrolyzed ***in situ*** to produce ceramic precursor particles. In such a case, the templating agent may be a polymer dispersion such as a latex as described above, or may be for example a silica or other inorganic material. The monodispersity of the green ceramic particles produced is able to confer substantial advantages in terms of mechanical properties, on the final fired ceramic material.

In yet a further embodiment, the templating agent may be an insoluble pigment particle (either organic or inorganic), and the non-aqueous phase may contain a film-forming polymer, as described above. The method of the invention may thus be used to prepare coated pigment particles, with accurate control over particle size and particle size distribution. The polymer film assists in providing controlled spacing of the pigment particles when a paint containing the pigment dries. This results in improved appearance to the finished surface. Because the thickness of the film-forming coating on the pigment particles may be determined very accurately, it is possible to choose the thickness of the film coating so as to provide particular optical effects, for example using optical interference to generate special colouring effects. Similarly, highly reflective or non-reflective coatings may readily be produced.

Emulsions produced in accordance with the method of the present invention can themselves be employed as templating agents for further processes in accordance with the present invention. Multi-layer coatings may thereby readily be provided. Incorporation of suitable

polymerizable monomers in one or more of such layers can be used to generate multiple polymer shells, each shell having predictable and defined properties. The ability to deposit a controlled thickness of non-aqueous phase in each deposition step gives rise to a number of desirable possibilities, such as the provision of different layers with different Tg values, so as for example to provide excellent adhesion together with good wear properties. Outermost layers can be produced with specific chemical functions to bind to specific surfaces, or to release from such surfaces, or with special optical effects, where successive layers are chosen for their refractive indices, or refractive index increments, to maximize or minimize the reflectivity and scattering power. Hollow cores may be provided to maximize such contrasts.

Alternatively, the properties of the various layers can be chosen so as to have specific rheological effects, in which the elasticity and viscosity of each layer is chosen so as to maximize or minimize the storage and loss components at different frequencies.

By the choice of components having appropriate electrical or mechanical properties, the resulting particles can be made to have novel electro-rheological or magneteo-rheological effects.

As indicated above, the method of the invention is particularly suitable for the preparation of pesticidal (e.g. herbicidal, insecticidal, fungicidal, or miticidal) emulsions.

Pesticidal substances suitable for use in the composition in accordance with the invention include

amitraz
azinphos-ethyl
azinphos-methyl
benzoximate
bifenthrin
binapacryl
bioresmethrin
chlorpyrifos
chlorpyrifos-methyl
cyanophos
cyfluthrin
cypermethrin
bromophos
bromopropylate
butacarboxim
butoxycarboxin
chlordimeform
chlorobenzilate
chloropropylate
chlorophoxim
fenamiphos
fenobucarb
gamma-HCH
methidathion
deltamethrin
dicofol
dioxabenzafos
dioxacarb
endosulfan
EPN
ethiofencarb
dinobuton
tetradifon
tralomethrin
N-2,3-dihydro-3-methyl-1,3-thiazol-2-ylidene-2,4-xylidene
parathion methyl
phosalone
phosfolan
phosmet
promecarb
resmethrin
temephos
tetramethrin
xylylcarb
acrinathrin
allethrin
benfuracarb
bioallethrin
bioallethrin S
bioresmethrin
buprofezin
chlorfenvinphos
chlorflurazuron
chlormephos
cycloprothrin
betacyfluthrin
cyhalothrin
cambda-cyhalothrin
alpha-cypermethrin
beta-cypermethrin
cyphenothrin
demeton-S-methyl
dichlorvos
disulfoton
edifenphos
empenthrin
esfenvalerate
ethoprophos
etofenprox
etrimphos
fenazaquin
fenitrothion
fenthiocarb
fenpropathrin
fenthion
fenvalerate
flucythrinate
flufenoxuron
tau-fluvalinate
formothion
hexaflumuron
hydroprene
isofenphos
isoprocarb
isoxathion
malathion
mephospholan
methoprene
methoxychlor
mevinphos
permethrin
phenothrin
phenthoate
pirimiphos-ethyl
pirimiphos-methyl
profenofos
propaphos
propargite
propetamphos
pyrachlofos
tefluthrin
terbufos
tetrachlorinphos
tralomethrin

triazophos
pyrachlofos
tefluthrin
terbufos
tetrachlorinphos
tralomethrin
triazophos

the following fungicides:-

benalaxyl
bupirimate
carboxin
dodemorph
dodine
fenarimol
ditalimfos
myclobutanil
nuarimol
oxycarboxin
penconazole
prochloraz
tolclofos-methyl
triadimefon
triadimenol
azaconazole
epoxyconazole
fenpropimorph
biteranol
cyproconazole
tetraconazole
difenoconazole
dimethomorph
diniconazole
ethoxyquin
etridiazole
fenpropidin
fluchloralin
flusilazole
imibenconazole
myclobutanil
propiconazole
pyrifenox
tebuconazole
tridemorph
triflumizole

the following herbicides:-

2,4-D esters
2,4-DB esters
acetochlor
aclonifen
alachlor
anilophos
benfluralin
benfuresate
bensulide
benzoylprop-ethyl
bifenox
bromoxynil esters
bromoxynil
butachlor
butamifos
butralin
butylate
carbetamide
chlornitrofen
chlorpropham
cinmethylin
clethodim
clomazone
clopyralid esters
CMPP esters
cycloate
cycloxydim
desmedipham
dichlorprop esters
diclofop-methyldiethatyl
dimethachlor
dinitramine
ethalfluralin
ethofumesate
fenobucarb
fenoxaprop ethyl
fluazifop
fluazifop-P
fluchloralin
flufenoxim
flumetralin
flumetralin
fluorodifen
fluoroglycofen ethyl

fluoroxypyr esters
flurecol butyl
flurochloralin
haloxyfop ethoxyethyl
haloxyfop-methyl
ioxynil esters
isopropalin
MCPA esters
mecoprop-P esters
metolachlor
monalide
napropamide
nitrofen
oxadiazon
oxyfluorfen
pendimethalin
phenisopham
phenmedipham
picloram esters
pretilachlor
profluralin
propachlor
propanil
propaquizafop
pyridate
quizalofop-P
triclopyr esters
tridiphane
trifluralin

Other pesticides such as the nitrification inhibitor nitrapyrin may also be employed. The compositions of the invention may also incorporate mixtures of two or more pesticides.

The pesticide may also be an organosoluble derivative of a pesticidal compound which is itself poorly organo-soluble or insoluble, such as cyhexatin dodecylbenzene-sulphonate.

The pesticidal compositions of the invention may also include optional adjuvants such as freezing point depressants preferably in amount of 0 percent to 15 percent, flow aids to prevent caking or aid in the re-dispersion of bottom sediment preferably in amounts of 0 percent to 5 percent, thickening agents preferably in amounts of 0 percent to 3 percent, and defoamers preferably 0 percent to 1 percent, to improve the overall properties under field storage and use conditions.

Similarly, conventional pesticide additives such as adjuvant solvents, surfactants for increasing penetration of the active substances or salts may be incorporated into the compositions to maintain or improve biological efficacy

of the composition. These may be incorporated into the oil phase or aqueous phase as appropriate.

In order to form an initial aqueous emulsion having the desired droplet size, it is necessary to employ an emulsifier (i.e. a surfactant). The emulsifier can be incorporated into the continuous (aqueous) phase (in which case the emulsifier preferably has a hydrophile-lipophile balance (HLB) number of 12 or more, usually from 12 to 20). Alternatively, the emulsifier may be incorporated into the disperse phase (in which case it preferably has an HLB number of less than 12).

Surfactants which can be advantageously employed herein as emulsifiers can be readily determined by those skilled in the art and include various nonionic, anionic, cationic, or amphoteric surfactants, or a blend of two or more surfactants may be employed. The surfactant employed for the emulsification of the non-aqueous phase should be compatible with the templating agent, and particularly if the templating agent is a latex, should be compatible with the latex, and with any surfactants which may be present in the latex composition.

Examples of suitable nonionic surfactants include polyalkylene glycol ethers, condensation products of alkyl phenols, aliphatic alcohols, aliphatic amines, or fatty acids with ethylene oxide, propylene oxide or mixtures of ethylene and propylene oxides (for example ethoxylated alkyl phenols or ethoxylated aryl or polyaryl phenols and carboxylic esters, solubilized with a polyol or polyoxyethylene) and polyvinyl alcohol/polyvinylactate copolymers.

Suitable cationic surfactants include quaternary

ammonium compounds and fatty amines.

Anionic surfactants include the oil-soluble (e.g. calcium, ammonium) salts of alkyl aryl sulphonic acids, oil soluble salts of sulphated polyglycolethers, salts of the esters of sulphosuccinic acid, or half esters thereof with nonionic surfactants and appropriate salts of phosphated polyglycolethers.

Preferred surfactants are those which form and stabilize oil-in-water emulsions such as ethoxylated alcohols, alkoxylated alkyl phenols, polyalkylene oxide copolymers and polyvinyl alcohol/polyvinylacetate copolymers. The surfactant is employed in an amount sufficient to ensure that the emulsion is easily formed and yet does not cause coagulation of the templating agent. This amount will generally be at least 1 percent and preferably from 2 percent to 15 percent, more preferably from 3 percent to 10 percent, and most preferably about 5 percent by weight of the total composition.

In a further alternative embodiment, the disperse phase may include a polymerizable material, such that after formation of the aqueous emulsion, the polymerizable material may be caused to polymerise, thereby generating microcapsules of a desired particle size distribution.

In a further alternative embodiment, the resulting emulsion particles may be caused to solidify after their formation by initially forming the emulsion at a temperature higher than that of the solidification temperature of the disperse phase, and subsequently cooling the emulsion produced to a temperature below the said solidification temperature.

The invention is illustrated by the following Examples. In the Examples, particle size and particle size distribution were determined using a Malvern Zetasizer or Malvern Mastersizer as appropriate. Data determined using the Mastersizer are given as "volume median diameter" (VMD), with an associated "span" as a measure of particle size distribution. Data determined using the Zetasizer are given as "Z-average mean", with an associated "polydispersity" figure, calculated as described in the instrument handbook.

EXAMPLE 1

An aqueous emulsion of styrene/butadiene copolymer (a latex) (12.5g dry weight) with a particle size 186nm and a polydispersity of 0.042 (by Malvern Zetasizer) was employed as a templating agent. The emulsion was mixed with water (39.3g) and a nonionic surfactant (Trade Mark Atlox 4991 - 5g) to give a total weight of 56.8g. To this was added under high shear an oil composed of chlorpyrifos (28g) and xylene (15.2g). After 10 seconds mixing, the product particle size was evaluated and found to be 276nm (with a polydispersity of 0.144). The calculated value for the particle size if all the oil phase was deposited around the polymer latex was 286nm.

EXAMPLE 2

An aqueous emulsion of styrene/butadiene copolymer (a latex) (12g dry weight) with a particle size 122nm and a polydispersity of 0.179 (by Malvern Zetasizer) was employed as a templating agent. The emulsion was mixed with water (43g) and a nonionic surfactant (Atlox 4991 - 5g) to give a total weight of 60g. To this was added under high shear an oil composed of chlorpyrifos (26g) and xylene (14g). After

10 seconds mixing, the product particle size was evaluated and found to be 191.7nm (with a polydispersity of 0.051). The calculated value for the particle size if all the oil phase was deposited around the polymer latex was 191nm.

EXAMPLE 3

The product of Example 2 above was taken (30g) and diluted to 60g with water (25g) and nonionic surfactant (Atlox 4991 - 5g). To this was added under high shear 40g of an oil composed of chlorpyrifos (26g) and xylene (14g). After 10 seconds mixing, the product particle size was evaluated (by Malvern Zetasizer) and found to be 293nm,with a poly-dispersity of 0.042. The calculated value for the particle size if all the oil phase was deposited about the previous oil/polymer composite was 289nm.

EXAMPLE 4

A polystyrene latex (6g dry weight) with a particle size of 980nm, and a span of 0.42 (by Malvern Mastersizer) was mixed with water (20g) and nonionic surfactant (Atlox 4991 - 5g). 25g aromatic solvent (Trade Mark Solvesso 200) was added and the mixture shaken and allowed to equilibrate. The particle size was measured and found to be 1640nm, with a span of 0.20. The calculated value for the particle size if all the oil phase was deposited about the latex was 1670nm.

EXAMPLE 5

A polystyrene latex (7g dry weight) with a particle size of 2250nm,and a span of 0.73 (by Malvern Mastersizer) was mixed with water and a mixture of nonionic surfactants

(Atlox 4991 1g and Atlox 4913 2g) to give a weight of 56g. To this was added a solution of chlorpyrifos (20g) in xylene (11g) in which was dissolved 3g polymethylene polyphenyl isocyanate (PAPI). The mixture was shaken and allowed to equilibrate until the product looked evenly coated with oil when evaluated microscopically. An interfacial polycondensation was effected by the addition of 1g diethylenetriamine in 9g water to yield a microcapsule composition containing 20.0% w/w chlorpyrifos. The particle size was measured and found to be 3700nm, with a span of 0.75 (by Malvern Mastersizer). The calculated value for the particle size if all the oil phase was deposited about the latex and then condensed to a capsule wall without shrinkage was 3870nm.

EXAMPLE 6

Example 5 was repeated without the inclusion of PAPI in the non-aqueous phase to produce an emulsion with a particle size, by microscopic examination of about 4000nm. The addition of dipropyleneglycol monomethylether as a co-solvent for the oil phase to wash it off the surface of the latex resulted in the immediate (within measurement time) appearance of the starting latex with a particle size of about 2000nm, confirming the ease with which the oil phase can be removed by a suitable co-solvent.

EXAMPLE 7

The particle size of a polystyrene latex was measured by the Zetasizer and the Hi-C instruments. This latex (208g) was then diluted with water (351g) and 50g of an alkoxylated nonylphenyl non-ionic surfactant (Trade Mark Renex 95). To the dispersion was added, with stirring 461g of a 65% w/w chlorpyrifos solution in xylene, sufficient to

produce a formulation containing 300g/l chlorpyrifos.

In a similar manner, a large quantity (692g) of a 65% chlorpyrifos solution in xylene, sufficient to produce a 450g/l chlorpyrifos formulation was added to a second dispersion containing the same latex, surfactant, and water (165g/50g/199g respectively). The particle size and polydispersity were determined by both Zetasizer and Hi-C instruments and a calculated vmd determined by the method of Example 6. The results are shown in Table 1.

Table 1

Sample	Hi-C vmd (nm)	polydispersity	Zetasizer (nm)	Calculated vmd (nm)
Example 7				
latex	141	0.06	152	--
300g/l	238	0.06	228	237
450g/l	292	0.077	262	283
Example 8				
latex	224	0.176	205	--
420g/l	455	0.165	341	455

EXAMPLE 8

The particle size of an ethylene/vinyl acetate/vinyl chloride terpolymer latex was measured by the Zetasizer and Hi-C instruments. This latex (140g) was then diluted with water (200g) and surfactant (Atlox 4991 - 50g) and to the dispersion was added, with stirring, 646g of a 65% w/w chlorpyrifos solution in xylene, sufficient to produce a formulation containing 420g/l chlorpyrifos. The particle

size, polydispersity and calculated vmd were determined as in Example 7. The results are shown in Table 1.

The particle size, polydispersity, and calculated vmd were determined as in Example 7.

Examples 7 and 8 illustrate that, in general, increase of particle size diameter occurs quantitatively corresponding to a deposition of the oil phase on the exterior of the particles. The low values noted for some of the Zetasizer measurements (particularly in Example 8) can be explained by the fact that some dissolution of the oil phase can take place during measurement with the Zetasizer, since measurement with this instrument typically takes place under higher dilution.

EXAMPLE 9

The chlorpyrifos microcapsule of Example 5 was tested for its biological effectiveness in two glasshouse trials. The comparison formulation, DURSBAN 4, was a commercially available 480g/l emulsifiable concentrate of chlorpyrifos. Both DURSBAN 4 and the sample of Example 5 were applied to test plants at various rates of application (given in mg chlorpyrifos/litre) and their efficacy against cotton leafworm and aphids was assessed as a T_0 (initial kill) and T_7 (kill after aging plants for 7 days in a controlled environment). The results are shown in Table 2. In a further trial, the effectiveness of the product of Example 5 against cotton leafworm over a 14 day period was evaluated. The results are also tabulated in Table 2.

Table 2 illustrates the effectiveness of the product of Example 5 against cotton leafworm and aphids where it is at least equivalent to DURSBAN 4 in knockdown (T_0 days) and

superior to DURSBAN 4 in residuality (T_7 days).

A further field comparison of Example 5 and DURSBAN 4 was conducted by spraying field plants with an emulsion of chlorpyrifos containing 20g of each product per 100 litres of water. The effectiveness of the treatment was evaluated by sampling treated leaves at from 0 to 12 days after application and allowing cotton leafworm larvae to feed on the leaves indicated an improved performance of Example 5 over time compared to DURSBAN 4. The results are shown in Table 3.

Table 2

Formulation	mg/litre	Cotton Leafworm % Mortality			Aphids % Mortality	
		T_o	T_7	T_{14}	T_o	T_7
DURSBAN 4	5	10	-	-	-	
	10	14	-	-	-	
	12.5	-	-	-	51	
	15	56	-	-		
	20	84	-	-	-	
	25	86	19	-	67	3
	50	-	24	24	93	7
	75	-	27	25	94	-
	100	-	56	52	100	13
	125	-	66	79	-	-
	150			77	-	-
	200			-	-	21
	400			-		47
				-		
Example 5	5	7	-	-	-	
	10	54	-	-	-	
	12.5	-	-	-	57	
	15	83	-	-	-	-
	20	100	-	-	-	23
	25	96	-	-	83	33
	50	-	80	100	93	-
	75	-	99	100	94	57
	100	-	99	100	100	-
	125	-	100	100	-	-
	150	-	100	99	-	80
	200	-	-	-	-	89
	400	-	-	-	-	

Table 3

	% mortality after X days (after treatment)									
days	0	1	3	4	5	6	7	8	9	12
DURSBAN 4	100	98.5	82	73.5	73.5	64.5	23	37	43	8.5
Example 5	100	100	100	100	92	91	76.5	72.5	65	19.5

The product of Example 5, despite being a capsule of about 4000nm in size showed no tendency to sediment, building a thixotropic structure which broke quickly on shaking without the need for any rheological additive, unlike other capsules of a similar nature but with broad particle size distribution (e.g. span > 2.0).

CLAIMS

1. A method of producing an aqueous emulsion having a dispersed non-aqueous phase with a substantially monodisperse particle size distribution, wherein the production of the emulsion is carried out in the presence of a dispersion of a templating agent and surfactant wherein the templating agent has a particle size distribution

   a) with a span of 1 or less, or

   b) such that its polydispersity is 0.1 or less, as measured by photo correlation spectroscopy,

and wherein the nature and amount of the surfactant is such as to cause deposition of the disperse phase on particles of the dispersed templating agent, such that the particle size distribution of the templating agent provides a template for the particle size distribution of the resulting emulsion.

2. A method of producing microcapsules, which method comprises preparing an aqueous emulsion having a continuous aqueous phase and a disperse phase, wherein the disperse phase contains a polymerisable material, and wherein the production of the emulsion is carried out in the presence of a surfactant and a dispersion of a templating agent, wherein the templating agent has a particle size distribution

   a) having a span of 1 or less, or

   b) such that the polydispersity of the templating agent is 0.15 or less as measured by photo correlation spectroscopy,

and wherein the templating agent and the surfactant are such that the deposition of the disperse phase of the emulsion takes place on particles of the dispersed templating agent, such that the particle size distribution of the templating agent provides a template for the

particle size distribution of the emulsion,

and polymerising the polymerisable material in the disperse phase of the emulsion to produce the said microcapsules.

3. A method as claimed in Claim 2 wherein the templating agent has a particle size distribution

a) with a span of 1 or less, or

b) such that its polydispersity is 0.1 or less as measured by photo correlation spectroscopy.

4. A method as claimed in Claim 2 or Claim 3, wherein the particle size distribution of the emulsion is multimodal.

5. A method as claimed in Claim 4, wherein the templating agent has a bimodal particle size distribution.

6. A method as claimed in any one of the preceding claims wherein the templating agent is a polymer latex.

7. A method as claimed in any one of the preceding claims, wherein the average particle size of the aqueous emulsion is 5 micrometers or less.

8. A method as claimed in any one of the preceding claims, wherein the disperse phase contains a volatile solvent, and wherein the method includes the step of volatilizing said solvent after the said deposition.

9. A method of producing an aqueous emulsion having a dispersed non-aqueous phase, wherein the production of the emulsion is carried out in the presence of a dispersion of a templating agent and surfactant characterized in that the nature and amount of the surfactant is such as to cause deposition of the disperse phase on particles of the dispersed templating agent, such that the particle size

distribution of the templating agent provides a template for the particle size distribution of the resulting emulsion, in that the disperse phase contains a volatile solvent, and in that the method includes the step of volatilizing said solvent after the said deposition.

10. A method as claimed in Claim 8 or Claim 9, wherein the volatile solvent is a hydrocarbon.

11. A method as claimed in any one of Claims 8 to 10, wherein the disperse phase contains a film-forming polymer, and wherein the method is carried out such that the volatile solvent is volatilized to produce a shell from the film-forming polymer.

12. A method as claimed in any one of the preceding claims, wherein the disperse phase comprises a pesticide.

13. A method as claimed in any one of the preceding claims, wherein the disperse phase is caused to solidify after the said deposition.

14. A method as claimed in Claim 13, wherein the said solidification is caused by cooling.

15. A method as claimed in any one of the preceding claims, wherein the said deposition is carried out by emulsifying the disperse phase in the presence of the templating agent.

16. A method as claimed in any one of Claims 1 to 14, wherein the said deposition is carried out by first preparing an aqueous emulsion of a non-aqueous material for providing the disperse phase, and subsequently combining the said aqueous emulsion with the templating agent so as to cause the said decomposition.

17. A method as claimed in any one of the preceding claims, wherein the templating agent constitutes from 10 to 50% by weight of the disperse phase of the final emulsion.

18. An emulsion or microcapsules produced by a process as claimed in any one of the preceding claims.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/08817

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N25/04 A01N25/28 B01F3/08 B01J13/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N B01F B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PESTICIDE SCIENCE, vol.29, no.4, 1990, BARKING GB pages 451 - 465 P.J. MULQUEEN ET AL. 'Recent development in suspoemulsions.' see paragraph 3.2 -paragraph 3.3; figures 1,2	1,6,7, 12,15-18
X	WO,A,89 03175 (DOW CHEMICAL CO.) 20 April 1989 cited in the application see page 11, line 8 - page 12, line 23	1,6,7, 12,15-18

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
14 November 1995	29.11.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Decorte, D

International Application No
PCT/US 95/08817

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 483 416 (AGFA-GEVAERT) 6 May 1992 cited in the application see page 2, line 58 - page 3, line 3 see page 2, line 11 see page 2, line 31 see claims ---	1,6-12, 16-18
A	EP,A,0 442 831 (RHONE-POULENC CHEMIE) 21 August 1991 ---	
A	EP,A,0 546 174 (MIYAZAKI-KEN) 16 June 1993 -----	

1

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No
PCT/US 95/08817

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-8903175	20-04-89	US-A-	5321049	14-06-94
		DE-A-	3875251	12-11-92
		DE-T-	3883251	25-11-93
		EP-A,B	0381691	16-08-90
		EP-A,B	0393069	24-10-90
		WO-A-	8903176	20-04-89
		JP-T-	3501845	25-04-91
		JP-T-	3501846	25-04-91
EP-A-0483416	06-05-92	DE-D-	69018079	27-04-95
		DE-T-	69018079	07-09-95
		JP-A-	5117401	14-05-93
		US-A-	5270354	14-12-93
EP-A-0442831	21-08-91	FR-A-	2658094	16-08-91
EP-A-0546174	16-06-93	WO-A-	9300156	07-01-93
		US-A-	5326484	05-07-94
		JP-A-	5220382	31-08-93